UNIVERSITI PUTRA MALAYSIA

EFFECTS OF VARIOUS BIOMOLECULES AND ULTRASONIC WAVE ON THE PHYSICO CHEMICAL PROPERTIES OF ZINC OXIDE SYNTHESIZED BY HYDROLYSIS METHOD

AHMAD ALFAIZ SHAPIEI.

EFFECTS OF VARIOUS BIOMOLECULES AND ULTRASONIC WAVE ON THE PHYSICO CHEMICAL PROPERTIES OF ZINC OXIDE SYNTHESIZED BY HYDROLYSIS METHOD

AHMAD ALFAIZ BIN SHAPIEI

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2005

EFFECTS OF VARIOUS BIOMOLECULES AND ULTRASONIC WAVE ON THE PHYSICO CHEMICAL PROPERTIES OF ZINC OXIDE SYNTHESIZED BY HYDROLYSIS METHOD

By

AHMAD ALFAIZ BIN SHAPIEI

Thesis Submitted in Fulfilment of the Requirement for the Degree of
Master of Science in the Faculty of Science
Universiti Putra Malaysia

2005

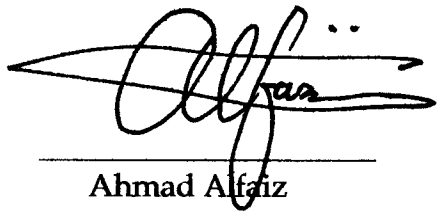
DEDICATION

In the absence of certainty, instinct is all you can follow.

This has been the fundamental that guided me in completing this thesis although the final deductions often comes by after some misunderstandings of the big picture, surprisingly. The thought of making this dissertation my own personal achievement is perhaps the main driven passion in completing this thesis. The other reason would be of a self assessment nature. Self assessment to oneself, setting back all that I've knew into a technically, structured and organized appraisal called the Master's Thesis; hopefully one up from the past experiences.

Ending my dedication with love and respect to my whole family members. May the force of truth will shine upon you always, InsyaAllah.

Sincerely from,



Ahmad Alfaiz

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

EFFECTS OF VARIOUS BIOMOLECULES AND ULTRASONIC WAVE ON THE PHYSICO CHEMICAL PROPERTIES OF ZINC OXIDE SYNTHESIZED BY HYDROLYSIS METHOD

By

AHMAD ALFAIZ BIN SHAPIEI

April 2005

Chairman: Professor Mohd Zobir bin Hussein, PhD

Faculty: Science

In this study, the effect of different biosubstrates on the physico-chemical properties of zinc oxide synthesized by the inorganic-organic agglomeration was characterized. The resulting materials containing layered ZnO was synthesized via hydrolysis mechanism between zinc nitrate precursor and the precipitator, sodium hydroxide at pH 10 in the presence of 0.10 M biosubstrates stabilized using the conventional thermal aging method. It was found that a pillared layered structure was formed when L-cystine biomolecule acting as a molecular propped, causing basal expansion of 10.1 Å, whereas other ZnO-biosubtrates agglomeration did not show any changes to the typical ZnO phase being observed based on the PXRD spectra obtained. Thus layered ZnO can be regarded as an inorganic vector or host structure in directing the physico-chemical transition of the layer ZnO-L-cystine in the agglomeration process whereby a lamellar solid is being formed. The phase transformation that consists of ZnO-L-cystine agglomerate was shown to have formed a significant chemical constituent with net L-cystine composition of 21 % and 37 % ex CHNS and EDX measurement

compared to the maximum of 5 % and 2 % obtained from other ZnO-biosubstrate agglomerations.

The intercalated ZnO-L-cystine agglomeration has a higher BET surface area of around 53 m^2/g with wider pore size distribution compared to between 4-34 m^2/g (with sharper pore size distribution pattern) of all other ZnO-biosubstrate agglomeration. The phase transformation of ZnO-fructose agglomerate however has shown to have a structure directing role in forming well divided monospherical microcrystallines. Together with other ZnO-biosubstrate agglomeration, it was observed that the degree of structural regularities based on it's surface morphology is in correlation to the Zn/O mole ratio obtained from EDX calculation whereby low Zn/O mole ratio was observed to display better crystallinity or higher order of ZnO-biosubstrate structural transformation.

Nonetheless, the influence of fructose biomolecule on the structural transformation was demonstrated further in a molar concentration gradient study, whereby grain-like surface morphology had nucleated into well divided monospheres in the crystal growing process as observed by SEM images from 0.01 M to 0.20 M fructose used. The final agglomerate at the highest molar concentration used (that yields monospherical morphology) was found to show a marked increase in net fructose composition at about 16 % from 6 % at it's lowest based on the EDX result. On the contrary, PXRD and FTIR data regarding the physico-chemical strata of the ZnO phase in the ZnO-fructose agglomerate remains unchanged.

Attemp to seek higher degree of structure-property feature of the ZnO-fructose agglomeration, sonification method was done using the accelerated aging process to activate the electronic state of the solid solution containing layer ZnO and fructose biomolecule in a series of ultrasonic exposure time gradient at 0.20 M fructose where stable micro spherical nucleation was observed earlier. It was found that the influence of ultrasonic irradiation was able to further doubles the net composition of fructose present (i.e. to 35 %) in the ZnO-fructose agglomeration compared to conventional thermal aging method as mentioned earlier. It was noticed also that an equally good surface morphology without any deformities was produced only at longer sonification period i.e. at the 60th minutes. In more, the surface area has also shown to exhibit an increasing trend from 1 to 4.7 m^2/g gaining higher pore volume or pore size distribution at longer sonification period due to higher chemical reactivity generated in the solid solution. The BET surface area however, was only half the surface area generated by the hydrothermally aged ZnO-fructose agglomeration of 9.4 m^2/g. The PXRD and FTIR data regarding the physico-chemical characteristic also shows that the ZnO phase in the ZnO-fructose agglomerate remains unchanged with the use of ultrasound.

Although no significant structural transformation or changes in the lattice orientation of the layer ZnO in the solid solution during ZnO-fructose agglomeration in the conventional or the accelerated synthesis method described, the effect of fructose on the structure directing role and inter-diffusion capability into the ZnO network is prevalent. It is also important to note that the increase in the porosity or pore profile of the ZnO-fructose aggregate due to the ultrasound is an additional aspect to enhance the structure-property relationship which was observed in this work.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGARUH PELBAGAI BIOMOLEKUL-BIOMOLEKUL DAN GELOMBANG ULTRASONIK TERHADAP SIFAT KIMIA FIZIKAL ZINK OKSIDA YANG DISINTESIS MELALUI KAEDAH HIDROLISIS

Oleh

AHMAD ALFAIZ BIN SHAPIEI

April 2005

Pengerusi : Professor Mohd Zobir Hussein, PhD

Fakulti : Sains

Dalam kajian ini, kesan pelbagai biomolekul terhadap sifat kimia-fizikal zink oksida yang telah disintesis dengan agelomerasi inorganik-organik telah dicirikan. Bahan yang terhasil yang mengandungi sebatian ZnO berlapis telah disintesiskan melalui mekanisma hidrolisis diantara zink nitrat dan agen pemendak, natrium hidroksida pada pH 10 dengan kehadiran 0.10 molar biosubstrat dan distabilkan dengan kaedah penuaan terma konvensional. Kajian menunjukkan bahawa struktur berlapis terpasak telah terbentuk apabila biomolekul L-cystine yang berfungsi sebagai sangga molekular mengakibatkan pengembangan jarak basal sebanyak 10.1 Å sementara agglomerasi ZnO-biosubstrat lain tidak menunjukkan sebarang perubahan pada fasa ZnO tipikal berdasarkan spektra PXRD yang diperolehi. Oleh yang demikian, ZnO berlapis bolehlah dianggap sebagai vektor inorganik atau struktur perumah yang mempengaruhi peralihan fiziko-kimia lapisan ZnO-L-cystine dalam proses agelomerasinya dimana suatu lamella pepejal telah terbentuk. Transformasi fasa yang mengandungi ZnO-L-cystine yang teragelomerasi telah membentuk suatu komposisi kimia dengan hasil

sebanyak 21 % dan 37 %, berdasarkan analisis CHNS dan EDX berbanding dengan 5 % dan 2 % maksima yang diperolehi daripada agelomerasi ZnO-biosubstrat lain.

Bagi bahan ZnO-L-cystine yang terinterkalasi, nilai luas permukaan BET yang lebih tinggi iaitu kira-kira 53 m^2/g dengan taburan saiz liang yang lebih luas telah diperolehi berbanding dengan 4-34 m^2/g (dengan taburan saiz liang yang lebih sempit) bagi bahan agelomerasi ZnO-biosubstrat yang lain. Walau bagaimana pun, transformasi fasa yang melibatkan ZnO-fruktos teragelomerasi didapati cenderung berperanan mengarah kepada pembentukan struktur dalam membentuk hablur mikro yang boleh menghablur secara sfera yang terasing antara satu sama lain. Bersamaan dengan agelomerasi ZnO-biosubstrat yang lain, kajian menunjukkan bahawa darjah keteraturan strukturnya berdasarkan morfologi permukaannya adalah berhubung dengan nisbah mol Zn/O yang dicerap dengan kiraan EDX dimana nisbah mol Zn/O yang rendah menunjukkan darjah penghabluran yang baik atau tingkatan tertinggi dalam transformasi struktur agelomerasi ZnO-biosubstrat.

Namun demikian, pengaruh biomolekul fruktosa terhadap transformasi struktur sebaliknya boleh ditunjukkan lagi dalam suatu kajian kesan kepekatan dimana morfologi permukaan seakan bijirin telah bernukleasi kepada sfera yang terasing dalam proses pertumbuhan hablur seperti yang dicerap pada imej SEM daripada tahap kepekatan 0.01 M sehingga 0.20 M fruktosa yang digunakan. Pada peringkat kepekatan fruktos yang tertinggi ini (yang menghasilkan morphologi mono sfera) telah menunjukkan peningkatan komposisi fruktosa yang tertinggi iaitu kira-kira 16 % daripada 6 % pada tahap yang paling rendah berdasarkan keputusan EDX. Sebaliknya,

data PXRD dan FTIR berkenaan sifat fiziko-kimia fasa ZnO dalam agelomerasi ZnO-fructose tidak menunjukkan apa-apa perbezaan.

Kajian selanjutnya untuk menunjukkan darjah tertinggi pada sifat hubungan diantara ciri dan struktur pada agelomerasi ZnO-fruktosa, kaedah sonifikasi telah digunakan untuk mempercepatkan proses penuaan larutan yang mengandungi ZnO dan biomolekul fruktos dalam satu siri masa pendedahan ultrasonik pada kepekatan fruktosa 0.20 M, dimana nukleasi berbentuk mikro sfera yang stabil telah dicerap. Keputusan menunjukkan bahawa pengaruh sinaran ultrasonik berupaya menggandakan komposisi fruktosa iaitu kepada 35 % dalam agglomerasi ZnO-fruktos berbanding dengan kaedah penuaan terma konvensional yang telah disebutkan sebelumnya. Adalah didapati bahawa morfologi permukaan yang setara tanpa apa-apa kecacatan dihasilkan pada masa sonifikasi yang panjang iaitu sehingga minit yang keenam puluh. Tambahan lagi luas permukaannya menunjukkan arah peningkatan iaitu daripada 1 hingga 4.7 m^2/g dan mencapai isipadu liang yang lebih tinggi atau taburan saiz liang yang lebih meluas pada sonifikasi yang lama disebabkan oleh penghasilan reaktiviti kimia yang tinggi dalam larutan pepejal tersebut. Luas permukaan BET ini adalah setengah daripada yang dihasilkan menurut kaedah penuaan terma agelomerasi ZnO-fruktosa iaitu 9.4 m^2/g.

Walaupun demikian, data PXRD dan FTIR berkenaan sifat fiziko-kimia fasa ZnO dalam agglomerasi ZnO-fruktosa masih tidak berubah walau pun dengan penggunaan ultrasonik. Walau pun tanpa perubahan transformasi struktur yang signifikan atau perubahan orientasi kekisi lapisan ZnO dalam larutan pepejal semasa agelomerasi ZnO-fruktosa pada kaedah konvensional mahu pun kaedah yang dipercepatkan, pengaruh fruktosa dalam mengarah

kepada penstrukturan dan keupayaan saling membaur kedalam rangkaian ZnO adalah nyata. Adalah penting untuk dinayatakan bahawa peningkatan porositi agelomerasi ZnO-fruktosa disebabkan kesan ultrasonik adalah aspek tambahan untuk meningkatkan hubungan antara sifat ciri-struktur yang telah dapat diperhatikan dalam kajian ini. .

ACKNOWLEDGEMENTS

This work of study is a synergistic product of many minds. The actual work began in the middle of 2003 as I was reviewing the presentation posted in the Science and Technology Seminar at the Palace of Golden Horses Hotel in Sri Kembangan during that time. I was moved by the first review that I've made on the "effect of various biomolecule on the layer ZnO" although experimentation work is still going on at that time with other approaches and methods to unleash the structure to property potential at the nanoscale level. I am grateful to the inspiration and insights from the many wisdom of the many thinkers that I have came by at the seminars either by their explanation, presentations and the exchange of ideas from short conversations either relevant or irrelevant.

I am also grateful to many students especially the Master students and the departmental staff who have assisted me in completing the many tasks that I need to fulfill. The experimental material and equipments rearrangements has also slowly open up new horizons in the work of my scientific studies.

For the production and development of this thesis itself I feel a deep sense of gratitude:

----- to my loving wife Ima and to each of our children Sofiya and Syafiq for bringing out the light and laughter in my living lives and not to mention the many sacrifices and support that all of you had given myself during these times.

------- to my father Shapiei and mother Nuraini for their constant interest, caring and insights.

--------- to Uncle Deedat for the sense of linguistic, literature and propagation.

-------- to Professor Mohd Zobir Hussein, Associate Professor Dr. Zulkarnain Zainal and Associate Professor Dr. Asmah Yahaya for the feedback, encouragement, editorial suggestions and production help.

-------- to my whole living descendants and the ones who have passed away for their sense of belonging and companionship.

-------- to the living memory of my past and current association with corporation/s for the sense of business purpose, products and services.

--------- to our nation for the sense of pride and direction that helped bring out the best in each of the people.

--------- to Universiti Putra Malaysia for granting myself the financial aid and the infrastructures in making this programme a success.

---------- to the many minds that have contributed in the form of journal publications, books and seminars.

---------- lastly, to God who inspired prophet Mohammad with the last revelation.

Alhamdulillah, the Lord be praised.

I certify that an Examination Committee met on 1st April 2005 to conduct the final examination of Ahmad Alfaiz bin Shapiei on his Master of Science thesis entitled "Effects of Various Biomolecules and Ultrasonic Wave on the Physico Chemical Properties of Zinc Oxide Synthesized by Hydrolysis Method" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Anuar Kassim, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Nor Azah Yusof, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mohd Ambar Yarmo, PhD
Associate Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(External Examiner)

GULAM RUSUL RAHMAT ALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

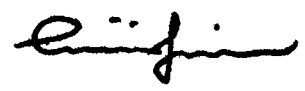
Date: 20 JUN 2005

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

Main Supervisor, PhD
Professor Dr. Mohd. Zobir bin Hussein
Faculty of Science,
University Putra Malaysia
(Chairman)

Co-Supervisor, PhD
Associate Professor Dr. Zulkarnain bin Zainal
Faculty of Science,
University Putra Malaysia
(Member)

Co-Supervisor, PhD
Associate Professor Dr. Asmah Yahaya
Faculty of Science,
University Putra Malaysia
(Member)

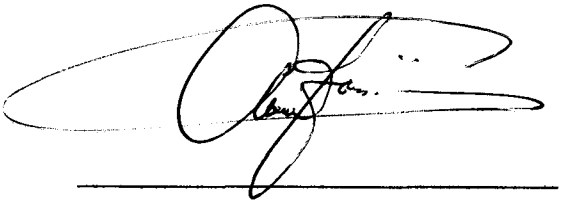


AINI IDERIS, PhD
Professor/ Dean
School of Graduate Studies
University Putra Malaysia

Date: 14 JUL 2005

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



AHMAD ALFAIZ BIN SHAPIEI

Date: 13th July 2005

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES